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(54) EPOXY COMPOSITIONS

(71) We, PPG INDUSTRIES, INC.,  
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15222, United States of America, (assignee of  
JOSEPH FRANK BOSSO and MARCO  
WISMER), do hereby declare the invention,  
for which we pray that a patent may be  
10 granted to us, and the method by which it is  
to be performed, to be particularly described  
in and by the following statement:—

The present invention relates to composi-  
tions containing synthetic resins which are  
15 water-dispersible epoxy resins.

Electrodeposition, although known for some  
time, has only recently become of commercial  
importance as a coating application method.  
Along with the increased use of such methods  
20 has been the development of certain composi-  
tions which can provide satisfactory coatings  
when applied in this manner. While many  
compositions can be electrodeposited, most  
coating compositions when applied using elec-  
trodeposition techniques do not produce com-  
25 mercially usable coatings. Moreover, electro-  
deposition of many coating materials, even  
when otherwise successful, is attended by  
various disadvantages such as non-uniform  
30 coatings and by poor throwing power. In  
addition, the coatings obtained are in most  
instances deficient in certain properties essen-  
tial for their utilization in many applications  
for which electrodeposition is otherwise suited.  
35 In particular, properties such as corrosion  
resistance and alkali resistance are difficult to  
achieve with the resins conventionally em-  
ployed in electrodeposition processes. This is  
especially true with the conventional electrode-  
40 position vehicles, which contain polycarboxylic  
acid resins solubilized with a base; their deposit  
on the anode and because of their acidic nature  
tend to be sensitive to common types of cor-  
rosive attack, e.g., by salt, alkali, etc. Many  
45 electrodeposited anodic coatings are subject  
to discoloration or staining because of dissolu-  
tion of metal ions at the anode.

Epoxy resins are among the most useful

resins for many purposes and have excellent  
corrosion resistance and other properties. They  
are employed in many coatings, but have not  
been employed in water-dispersible composi-  
tions suitable for application by electrodeposi-  
50 tion because they could not be adequately dis-  
persed in water under the conditions required  
in such processes. Esterified epoxies have been  
utilized, but these act similarly to the poly-  
55 carboxylic acid resins, and while offering many  
advantages over such polycarboxylic acid  
resins, are still subject to many of their dis-  
advantages.

It has now been found that synthetic resins  
which are ungelled, water-dispersible epoxy  
resins have epoxy groups, chemically-bound  
quaternary ammonium base groups, and in  
65 some cases oxyalkylene groups, can be easily  
utilized to provide clear or colloidal water  
solutions. "Chemically-bound", as utilized,  
herein, includes salts as well as covalent bond-  
ing. These compositions, when solubilized with  
70 an acid having a dissociation constant greater  
than about  $1 \times 10^{-5}$ , do not require the pre-  
sence of oxyalkylene groups, which may then  
be optionally present. The compositions de-  
scribed herein can be applied by electrodeposi-  
75 tion to provide adherent coatings which have  
excellent properties. When electrodeposited,  
they deposit on the cathode. When employed  
in aqueous compositions for electrodeposition,  
the above resins form the major resinous con-  
80 stituent of the composition, either as the sole  
resinous component or along with one or more  
other resinous or film-forming materials. Among  
the properties of the coatings herein are the  
desirable properties ordinarily associ-  
85 ated with electrodepositable resins known her-  
etofore, and, in addition, these reaction pro-  
ducts provide coatings of valuable advantages  
and properties. These include a high level of  
90 resistance to salt spray, alkali and similarly  
corrosive elements, even over unprimed metals  
and in the absence of corrosive inhibiting pig-  
ments, and are resistant to staining and dis-  
coloration which is often encountered with  
95 electrodeposited coatings based on anodic-type  
resins. These resins, with or without oxy-

[Price 33p]

alkylene groups, when solubilized with an acid having a dissociation constant greater than  $1 \times 10^{-3}$ , have appreciably higher throw paper and better film-forming characteristics than in similar compositions, for example, those described in U.S. Patent No. 3,301,804.

The resins of the invention are ungelled, water-dispersible epoxy resins having in their molecule more than 1,2-epoxy group per average molecule and containing chemically-bound quaternary ammonium base salts, the quaternary ammonium base salts being salts of boric acid and/or an acid having a dissociation constant greater than boric acid, including organic and inorganic acids. Where the salt is a salt of an acid having a dissociation constant less than  $1 \times 10^{-3}$ , the resin should contain from about one percent to 90 percent or more of oxyalkylene groups. When the resin is devoid of oxyalkylene groups, upon solubilization, at least a portion of the salt must be a salt of an acid having a dissociation constant greater than  $1 \times 10^{-3}$ . Preferably, the acid is an organic, carboxylic acid. The presently preferred acid is lactic acid. Preferably the resins contain at least 0.05% by weight and from preferably 0.05 to 16 percent by weight of nitrogen and at least 1 percent of said nitrogen and preferably at least 20 percent, more preferably, at least 50 percent, and most preferably, substantially all, of the nitrogen being in the form of a chemically-bound quaternary ammonium base salt groups; preferably the remainder of said nitrogen being in the form of amino nitrogen.

The epoxy compound from which the resins of the invention may be derived can be any monomeric or polymeric compound or mixture of compounds having a 1,2-epoxy equivalency greater than 1.0, that is, in which the average number of 1,2-epoxy groups per molecule is greater than 1. It is preferred that the epoxy compound be resinous, that is, a polyepoxide, i.e., containing more than one epoxy group per molecule. The polyepoxide can be any of the well-known epoxides, provided it contains sufficient epoxy groups so that some residual epoxy groups remain in the product after the oxyalkylation for reaction with the amine compound described hereinafter. Examples of these polyepoxides have, for example, been described in U.S. Patents Nos. 2,467,171; 2,615,007; 2,716,123; 3,030,336; 3,053,855 and 3,075,999. A useful class of polyepoxides are the polyglycidyl ethers of polyphenols, such as Bisphenol A. These may be produced, for example, by etherification of a polyphenol with epichlorohydrin or dichlorohydrin in the presence of an alkali. The phenolic compound may be bis(4-hydroxyphenyl)-2,2-propane, 4,4'-dihydroxybenzophenone, bis(4-hydroxyphenyl)-1,1-ethane, bis(4-hydroxyphenyl)-1,1-isobutane; bis(4-hydroxy-tertiarybutylphenyl)-2,2-propane, bis(2-hydroxynaphthyl)methane or 1,5-dihydroxy-

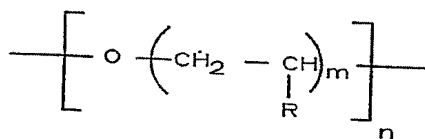
naphthalene. Another quite useful class of polyepoxides are products similar from novolak resins or similar polyphenol resins.

Also suitable are the similar polyglycidyl ethers of polyhydric alcohols which may be derived from such polyhydric alcohols as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, 1,5-pentanediol, 1,2,6-hexanetriol, glycerol and bis(4-hydroxycyclohexyl)-2,2-propane.

There can also be used polyglycidyl esters of polycarboxylic acids which are produced by the reaction of epichlorohydrin or a similar epoxy compound with an aliphatic or aromatic polycarboxylic acid, such as oxalic acid, succinic acid, glutaric acid, terephthalic acid, 2,6-naphthylene dicarboxylic acid and dimerized linolenic acid. Examples are diglycidyl adipate and diglycidyl phthalate.

Also useful, are polyepoxides derived from the epoxidation of an olefinically unsaturated alicyclic compound. Included are diepoxides comprising in part one or more monoepoxides. These polyepoxides are non-phenolic and are obtained by epoxidation of alicyclic olefins, for example, by oxygen and selected metal catalysts, by perbenzoic acid, by acetaldehyde monoperacetate, or by peracetic acid. Among such polyepoxides are the epoxyalicyclic ethers and esters, which are well known in the art.

Where the resin of the invention contains oxyalkylene groups, they can be derived from polyepoxides containing oxyalkylene groups in the epoxy molecule. Such oxyalkylene groups are typically groups of the general formula:



where R is hydrogen or alkyl, preferably lower alkyl (e.g., having 1 to 6 carbon atoms) and where, in most instances, m is 1 to 4 and n is 2 to 50. Such groups can be pendent to the main molecular chain of the polyepoxide or part of the main chain itself. The proportion of oxyalkylene groups in the polyepoxide depends upon many factors, including the chain length of the oxyalkylene group, the nature of the epoxy of the degree of water solubility desired. Usually the epoxy contains at least 1 percent by weight or more, and preferably 5 percent or more, of oxyalkylene groups.

Some polyepoxides containing oxyalkylene groups are produced by reacting some of the epoxy groups of a polyepoxide, such as the epoxy resins mentioned above, with a monohydric alcohol containing oxyalkylene groups. Such monohydric alcohols are conveniently produced by oxyalkylating an alcohol, such as

methanol, ethanol, or other alkanol, with an alkylene oxide. Ethylene oxide, 1,2-propylene oxide and 1,2-butylene oxide are especially useful alkylene oxides. Other monohydric alcohols can be, for example, the commercially available materials known as Cellosolves and Carbitols ("Cellosolve" and "Carbitol" are registered Trade Marks) which are mono-alkyl ethers of polyalkylene glycols. The reaction of the monohydric alcohol and the polyepoxide is generally carried out in the presence of a catalyst; formic acid, dimethylethanolamine, diethylethanolamine, N,N-dimethylbenzylamine and, in some cases, stannous chloride are useful for this purpose.

Similar polyepoxides containing oxyalkylene groups can be produced by oxyalkylating the epoxy resin by other means, such as by direct reaction with an alkylene oxide.

The polyepoxide employed to produce the foregoing epoxides containing oxyalkylene groups can contain a sufficient number of epoxy groups so that the average number of residual epoxy groups per molecule remaining in the product after the oxyalkylation is greater than 1.0. Where oxyalkylene groups are present, the epoxy resin preferably contains from 1.0 to 90 percent or more by weight of oxyalkylene groups.

It should be noted that the polyoxyalkylene compound reacted need not be water-soluble or dispersible. It has been shown that relatively high molecular weight polyoxyalkylene compounds, water-insoluble *per se*, when reacted in the manner of the invention, render the final product more water-dispersible.

There can also be utilized combinations for the foregoing, either as mixtures of epoxy compounds or by providing pendent oxyalkylene groups on the polyepoxide containing such groups in its main chain.

Other epoxy-containing compounds and resins include nitrogeneous diepoxides such as disclosed in U.S. 3,365,471; epoxy resins from 1,1-methylene bis(5-substituted hydantoin), U.S. 3,391,097; bis-imide containing diepoxides, U.S. 3,450,711; epoxylated aminomethyldiphenyl oxides, U.S. 3,312,664; heterocyclic N,N-diglycidyl compounds, U.S. 3,503,979; amino epoxy phosphonates, British Patent No. 1,172,916; 1,3,5-triglycidyl isocyanurates, as well as other epoxy-containing materials known in the art.

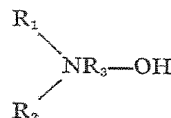
The resins of the invention can be formed by reacting the epoxy compound with an amine salt to form quaternary amine base group-containing resins.

Examples of amines whose salts may be employed include ammonia; primary, secondary or tertiary amines; and preferably tertiary amines. Specific amines include dimethylethanolamine, diethylethanolamine, trimethylamine, triethylamine, diethylamine, dipropylamine and 1-amino-2-propanol. The amines may be unsubstituted amines or amines sub-

stituted with non-interfering groups such as halogen or hydroxyl. The salts may be salts of boric acid or an acid having a dissociation constant greater than that of boric acid and preferably an organic acid having a dissociation constant greater than about  $1 \times 10^{-5}$ . The presently preferred acid is lactic acid. Such acids include boric acid, lactic acid, acetic acid, propionic acid, butyric acid, hydrochloric acid, phosphoric acid, sulphuric acid. Also included are ammonium borate, ammonium lactate, ammonium acetate, ammonium chloride, ammonium phosphate, as well as other amine and ammonium salts as set out above.

A distinct class of amines within the broader class are amines containing one or more secondary or tertiary amino groups and at least one hydroxyl group.

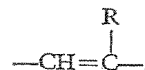
In most cases the hydroxyl amine employed corresponds to the general formula:



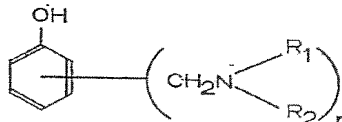
where  $R_1$  and  $R_2$  are alkyl, aryl, alkaryl or aralkyl groups such as methyl, ethyl or benzyl.  $R_1$  can also be hydrogen. The nature of the particular groups is less important than the presence of a secondary or tertiary amino nitrogen atom. The group represented by  $R_3$  is a divalent organic group, such as alkylene or substituted-alkylene, e.g., oxyalkylene or poly(oxyalkylene), or, less desirably, arylene, alkarylene or substituted arylene.  $R_3$  can also be an unsaturated group, e.g., an alkylene group such as



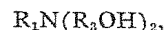
or



Other groups represented by  $R_3$  include cyclic or aromatic groups; one type of useful amine, for instance, is represented by the formula:



where  $n$  is 1 to 3. Dialkanolamines, of the general formula



and trialkanolamines, of the general formula

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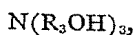
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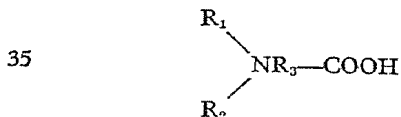


are also useful.

Some examples of specific amines are as follows:

- 5 dimethylethanolamine  
dimethylpropanolamine  
dimethylisopropanolamine  
dimethylbutanolamine  
diethylethanolamine  
10 ethylethanolamine  
methylethanolamine  
N-benzylethanolamine  
diethanolamine  
triethanolamine  
15 dimethylaminomethyl phenol  
tris(dimethylaminomethyl)phenol  
2-[2-(dimethylamino)ethoxy]ethanol  
1 - [1 - (dimethylamino) - 2 - propoxy] -  
2-propanol  
20 2 - (2 - [2 - (diethylamino)ethoxy] -  
ethoxy)ethanol  
1 - [2 - (dimethylamino)ethoxy] - 2 -  
propanol  
1 - [1 - (dimethylamino) - 2 - propoxy] -  
25 2-propoxy)-2-propanol

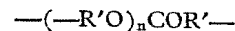
Another distinct class of amines within the broader class are amines containing one or more secondary or tertiary amino groups and at least one terminal carboxyl group. These amines can in themselves act as amine salts since the carboxyl group can form an internal salt as further explained below. In most cases where a carboxyl amine is employed, it corresponds to the general formula:



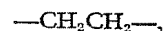
where  $R_1$ ,  $R_2$  and  $R_3$  are as defined above.

- Such amines can be prepared by known methods. For example, an acid anhydride, such as succinic anhydride, phthalic anhydride, 40 or maleic anhydride, can be reacted with an alkanolamine, such as dimethylethanolamine or methyldiethanolamine; the group represented by  $R_3$  in the amines produced in such cases contain ester groups. Other types of amines are provided, for example, by reacting an 45 alkylamine with an alkyl acrylate or methacrylates such as methyl or ethyl acrylate or methacrylate as described in U.S. Patent No. 3,419,525. Preferably the ester group is subsequently hydrolyzed to form a free carboxyl group. Other methods for producing amines 50 of different types can also be employed.

- It can be seen that the groups represented by  $R_3$  can be of widely varying types; some 55 examples are:



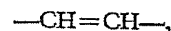
where each  $R'$  is alkylene, such as



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etc., or alkylene, such as



and  $n$  is 2 to 10 or higher. Other groups represented by  $R'$  include cyclic or aromatic groups.

Some examples of specific amines are as follows:

- N,N-dimethylaminoethyl hydrogen maleate  
N,N-diethylaminoethyl hydrogen maleate  
N,N-dimethylaminoethyl hydrogen succinate  
N,N-dimethylaminoethyl hydrogen phthalate  
N,N - dimethylaminioethyl hydrogen hexa -  
hydrophthalate  
2 - (2 - dimethylaminoethoxy)ethyl hydro- 75  
gen maleate  
1 - methyl - 2 - (2 - dimethylaminoeth -  
oxy)ethyl hydrogen maleate  
2 - (2 - dimethylaminoethoxy)ethyl hydro-  
gen succinate 80  
1,1 - dimethyl - 2 - (2 - dimethylaminoeth -  
oxy)ethyl hydrogen succinate  
2 - [2 - (2 - dimethylaminoethoxy) -  
ethoxy]ethyl hydrogen maleate  
beta-(dimethylamino)propionic acid 85  
beta-(dimethylamino)isobutyric acid  
beta-(diethylamino)propionic acid  
1 - methyl - 2 - (dimethylamino)ethyl  
hydrogen maleate  
2 - (methylamino)ethyl hydrogen succinate 90  
3-(ethylamino)propyl hydrogen maleate  
2-[2-(dimethylamino)ethoxy]ethyl hydro-  
gen adipate  
N,N - dimethylaminoethyl hydrogen azelate  
di - (N,N - dimethylaminoethyl)hydrogen 95  
tricarballylate  
N,N - dimethylaminoethyl hydrogen itacon-  
ate  
1 - (1 - [1(dimethylamino) - 2 - pro -  
poxyl - 2 - propoxyl - 2 - propyl hydrogen 100  
maleate  
2 - [2 - (2 - [2 - dimethylamino)ethoxyl -  
ethoxy]ethoxy)ethyl hydrogen succinate
- In one embodiment, the epoxy compounds described above may be reacted with a tertiary 105 amine salt of boric acid to produce the epoxy reaction products of the invention.
- The amine salts and the epoxy compound

are reacted by mixing the components, usually at moderately elevated temperatures such as 70—110°C. Alternatively, in a less preferred embodiment in the case of a tertiary amine, the amine may be added to the epoxy compound and the acid utilized to form the appropriate salt may be subsequently added, even as late as the solubilization step. A solvent is not necessary, although one is often used in order to afford better control of the reaction. Aromatic hydrocarbons or monoalkyl ethers of ethylene glycol are suitable solvents. The proportions of the amine salt and the epoxy compound can be varied and the optimum proportions depend upon the particular reactants. Ordinarily, however, from about one part to 50 parts by weight of the salt per 100 parts of epoxy compound is employed. The proportions are usually chosen with reference to the amount of nitrogen, which is typically from 0.05 to 16 percent based on the total weight of the amine salt and the epoxy compound. Preferably there are utilized from 3 parts to 30 parts of salt per 100 parts of epoxy compound or from 0.1 to 3 percent of nitrogen. Since the amine salt reacts with the epoxide groups of the epoxy resin employed, in order to provide an epoxy group-containing resin, the stoichiometric amount of amine employed should be less than the stoichiometric equivalent of the epoxide groups present, so that the final resin is provided with at least one epoxy group per average molecule.

The particular reactants, proportions and reaction conditions should be chosen in accordance with considerations well-known in the art, so as to avoid gellation of the product during the reaction. For example, excessively severe reaction conditions should not be employed. Similarly, compounds having reactive substituents should not be utilized along with epoxy compounds with which those substituents might react adversely at the desired conditions.

The product forming the resin of the invention may be crosslinked to some extent; however, it remains soluble in certain organic solvents and can be further cured to a hard, thermoset state. It is significantly characterized by its epoxy content and chemically-bonded quaternary ammonium salt content.

Aqueous compositions containing the above reaction products are highly useful as coating compositions and can be applied by any conventional method, such as by dipping, brushing, etc. They are, however, eminently suited to application by electrodeposition.

Where the resin of the invention was prepared employing at least in part a salt of an acid having a dissociation constant greater than  $1 \times 10^{-5}$ , it was not necessary to add a solubilizing agent to the product to obtain a suitable aqueous electrodepositable composition, although an acid or acidic solubilizing agent can be added if desired. Where boric

acid salts as described above are employed to prepare the resin without the presence of a salt of an acid having a dissociation constant greater than  $1 \times 10^{-5}$  and the resin does not contain oxyalkylene groups, compositions within the scope of the invention can be prepared by adding such an acid, the stronger acid replacing the boron compound in the resin, a weaker salt in the resin, and the boron compound forming substantially undissociated boric acid, remaining in aqueous media and being at least partially co-deposited with the resin.

The presence of a boron compound in the electrodeposited film is of substantial benefit in that boron compounds apparently catalyze the cure of the deposited film, allowing lower cure temperatures and/or harder films.

The acid or acidic solubilizing agent may be any acid having a dissociation constant greater than  $1 \times 10^{-5}$ . Preferably, the acid or acidic solubilizing agent should be an organic acid having a dissociation constant greater than  $1 \times 10^{-5}$ , the presently preferred acid being lactic acid. The addition of acid aids in stabilizing the resin, since the epoxy may tend to further polymerize on storage under highly alkaline conditions; in some cases, the acid also helps to obtain more complete dissolution of the resin. It is also desirable to electrodeposit these coatings from an acidic or only slightly basic solution (e.g., having a pH between 3 and 8.5), and the addition of acid thus is often useful to achieve the desired pH.

Where a carboxyl amine is employed in forming the resins of the invention, the resultant resin contains a zwitterion, or internal salt, that is, an interaction between the quaternary group formed and the carboxyl group present, the carboxyl group displaying a dissociation constant greater than  $1 \times 10^{-5}$ . The resultant resin is inherently self-solubilized without the use of external solubilizing agents.

The resin of the invention, when placed in a water-containing medium, such as an electrodeposition high solids feed concentrate or the electrodeposition bath, changes character. Since frequently, the boron, if present, is apparently weakly chemically-bound in the resin, it is subject to cleavage from the resin molecule and, while the boron electrodeposits with the resin and is found in the electrodeposited film, the boron may be removed from the water-containing medium in whole or in part by separation means, such as electro-dialysis or ultrafiltration, in the form of boric acid.

Thus, the invention also includes aqueous dispersions comprising an ungelled water-dispersed epoxy resin having at least one 1,2-epoxy group per average molecule, and chemically-bound quaternary ammonium base salts. The resin contains at least 0.05% and preferably 0.05 to 16 percent by weight nitrogen, at least one percent of said nitrogen and

preferably at least 20 percent, more preferably at least 50 percent, and most preferably, substantially all of the nitrogen being in the form of chemically-bound quaternary ammonium base salt groups; and when said ammonium base salt is of an acid having a dissociation constant of  $1 \times 10^{-5}$  or less, the resin contains at least 1 per cent by weight of oxyalkylene groups. Preferably, the remainder of said nitrogen being in the form of amino nitrogen, preferably tertiary amine nitrogen, said water-containing medium containing in the preferred embodiment from 0.01 to 8 percent by weight of boron metal present as boric acid and/or borate or boric acid complex.

The concentration of the product in water depends upon the process parameters to be used and is, in general, not critical, but ordinarily the major proportion of the aqueous composition is water, e.g., the composition may contain from one to 25 percent by weight of the resin.

Preferably, the electrodepositable compositions of the invention contain a coupling solvent. The use of a coupling solvent provides for improved deposited film appearance. These solvents include hydrocarbons, alcohols, esters, ethers, and ketones. The preferred coupling solvents include monoalcohols, glycols, and polyols as well as ketones and ether alcohols. Specific coupling solvents include isopropanol, butanol, isophorone, Pentoxane (registered Trade Mark) (4-methoxy-4-methyl pentanone-2), ethylene and propylene glycol, the monomethyl, monoethyl and monobutyl ethers of ethylene glycol, 2-ethylhexanol, and hexyl Cellosolve ("Cellosolve" is a registered Trade Mark). The presently preferred coupling solvent is 2-ethylhexanol. The amount of solvent is not unduly critical, generally between about 0.1 percent and about 40 percent by weight of the dispersant may be employed, preferably between about 0.5 to about 25 percent by weight of the dispersant is employed.

While the resins hereinabove described may be electrodeposited as substantially the sole resinous component of the electrodeposited composition, it is frequently desirable in order to improve or modify film appearance and/or film properties, to incorporate into the electrodepositable compositions various non-reactive and reactive compounds or resinous materials such as plasticizing material including N-cyclohexyl-p-toluene sulfonamide, ortho- and para-toluene sulfonamide, N-ethyl-ortho- and para-toluene sulfonamide, aromatic and aliphatic polyether polyols, phenol resins including allyl ether containing phenolic resins, liquid epoxy resins, quadrols, polycaprolactones; triazine resins such as melamine-based resins and benzoguanamine-based resins, especially alkylated formaldehyde reaction products thereof; urea formaldehyde resins, acrylic resins, hydroxy and/or carboxyl

group-containing polyesters and hydrocarbon resins.

Other materials include esters such as butylbenzyl phthalate, dioctyl phthalate, methyl phthalylethyl glycolate, butylphthalylbutyl glycolate, cresyl diphenyl phosphate, 2-ethylhexyl diphenyl phosphate, polyethylene glycol 200 dibenzoates as well as polyesters, 2,2,4-trimethyl pentanediol monoisobutyrate (Texanol, registered Trade Mark).

In most instances, a pigment composition and, if desired, various additives such as anti-oxidants, surfactants, or wetting agents, for example, Foam Kill 639 (a hydrocarbon oil-containing inert diatomaceous earth), as well as glycolated acetylenes (the Surfynols, for example), sulfonates, sulfated fatty amides, and alkylphenoxypolyoxyalkylene alkanols are included. The pigment composition may be of any conventional type, comprising, for example, iron oxides, lead oxides, strontium chromate, carbon black, titanium dioxide, talc, barium sulfate, as well as color pigments such as cadmium yellow, cadmium red and chromic yellow.

In the electrodeposition processes employing the aqueous coating compositions described above, the aqueous composition is placed in contact with an electrically-conductive anode and an electrically-conductive cathode, with the surface to be coated being the cathode, while in contact with the bath containing the coating composition, an adherent film of the coating composition is deposited on the cathode. This is directly contrary to the processes utilizing polycarboxylic acid resins, as in the prior art, and the advantages described are, in large part, attributed to this cathodic deposition.

The conditions under which the electrodeposition is carried out are, in general, similar to those used in electrodeposition of other types of coatings. The applied voltage may be varied greatly and can be, for example, as low as one volt or as high as several thousand volts, although typically between 50 and 500 volts. The current density is usually between 1.0 ampere and 15 amperes per square foot, and tends to decrease during electrodeposition.

The resin of the invention when freshly electrodeposited on the cathode contains quaternary ammonium base groups. The acid moiety which forms the salt migrates at least in part towards the anode. Where the electrodeposition bath contains boron, the electrodeposited resin further contains boron which is bonded with the basic groups present in the film which has electrodeposited upon the cathode. The amounts of bonded boron in the electrodeposited film increase with increasing boron concentration in the bath to a saturation value, dependent on the number of basic groups in the concentration and the basicity of the base groups.

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The film, while it may be crosslinked to some extent, remains soluble in certain organic solvents.

5 The freshly-deposited, uncured electrodeposited film may be characterized as follows: an epoxy resin electrodeposited upon an electrically-conductive substrate comprising an ungelled epoxy resin having at least one  
10 1,2-epoxy group per average, molecule, chemically-bound quaternary ammonium base, and where the electrodepositable composition does not contain an acid having a dissociation constant greater than  $1 \times 10^{-5}$ , at least 1 percent of oxyalkylene groups. Where boron is  
15 present in the electrodepositable composition, 0.01 to 8 percent by weight or boron in the form of quaternary and amine borates and boron complexes.

20 The method of the invention is applicable to the coating of any conductive substrate, and especially metals such as steel, aluminum, copper and magnesium. After deposition, the coating is cured, usually by baking at elevated temperatures. Temperatures of 250°F. to  
25 500°F. for one to 30 minutes are typical baking schedules utilized.

During the cure, especially at elevated temperatures, at least a substantial portion of the quaternary ammonium base decomposes to tertiary amine nitrogen, which aids in the crosslinking of the coating, which upon curing is infusible and insoluble. The presence of boron salts and complexes in the film increases the rate of crosslinking, reduces the temperatures  
30 necessary for acceptable curing in commercially-reasonable times and produces coatings with improved hardness and corrosion resistance.

35 The resin constituents may be qualitatively and quantitatively determined by numerous methods known in the art.

Epoxy groups may be determined by the well-known pyridinium hydrochloride method as described, for example, in Siggia, "Quantitative Organic Analysis via Functional Groups", John Wiley & Sons, Inc., New York (1963), page 242.

40 The total base groups present in the polymer, that is, quaternary and amine groups present, may be determined on a separate resin sample. Usually the resin sample will be neutral. If, however, the resin is basic, the sample should be neutralized with a known amount of the acid present in the resin as a salt. Where the acid present in the resin as a salt is a weak acid as compared to HCl, the resin is titrated with HCl and back-titrated with sodium hydroxide on an automatic titrator. The HCl titration yields the total  
45 base groups present. The sodium hydroxide back-titration distinguishes quaternary groups from amine groups. For example, a typical analysis is conducted as follows: a 10 milliliter sample of an about 10 percent solids  
50 electrodeposition bath is pipetted in 60 milli-

liters of tetrahydrofuran. The sample is titrated with 0.1000 normal HCl to the pH end point. The amount of standard acid used is equivalent to the quaternary base and amine equivalents present. The sample is then back  
55 titrated with 0.1000 normal sodium hydroxide to give a titration curve with multiple end points. In a typical instance, the first end point corresponds to excess HCl. From the HCl titration, the second end point corresponds to the neutralization of the weak acid (for example, lactic acid) and amine hydrochloride. The difference in volume between the two endpoints gives the volume of standard base equivalent to the weak acid and amine content of the sample.

Whereas solvent such as propylene glycol is employed with, for example, tetrahydrofuran to maintain sample homogeneity, boron present will also titrate since the boron in the form present forms an acid complex with the propylene glycol. Under the conditions specified, the boric acid may be distinguished from the weak acid (e.g., lactic) by an additional inflection point in the pH titration curve. Depending on the strength of the amine group present, it may be included either in the weak acid (e.g., lactic) or boric acid portion of the titration curve.

Excess weak acid or amine salt in the electrodeposition bath may be determined by alcoholic-KOH titration. For example, a 10 milliliter sample of about 10 percent solids electrodeposition bath is pipetted into 60 milliliters of tetrahydrofuran and potentiometrically titrated with 0.1000 normal alcoholic KOH to the first end point. The amount of KOH consumed is equivalent to any acid or amine salt in the sample. In the case of neutral compositions, KOH titration is a measure of the amount of amine present in the form of amine salt since the quaternary, being a strong base, will not titrate.

In the case of the presence of acid salts of strong acids, other methods must be employed to determine acid, amine and quaternary groups present. For example, where the resin contains amine hydrochloride and quaternary hydrochloride groups, the resin may be dispersed, for example, in a mixture of glacial acetic acid and tetrahydrofuran, the chloride complexed with mercuric acetate and the sample titrated with perchloric acid to yield the total amine and quaternary groups. Separate alcoholic KOH titration will yield the amine groups present since the quaternary is of comparable strength to the alcoholic KOH.

Boron may be determined as described by R. S. Braman, "Boron Determination", Encyclopedia of Industrial Chemical Analysis, F. D. Snell and Hilton, Editors, John Wiley & Sons, Inc., New York (1968), Volume 7, pages 384-423. The boron may be determined on a separate sample. For example, by

pipetting a 10 milliliter sample of an approximately 10% solid cationic electrodeposition bath into 60 milliliters of distilled water. Sufficient HCl is then added to lower the pH to about 4.0. The sample is then back-titrated with 0.1000 normal sodium hydroxide, using a Metrohm (registered Trade Mark) potentiograph E-436 automatic titrator or equivalent apparatus, to the first inflection point in the pH titration curve. There is then added 7 grams of mannitol. The solution becomes acid and titration is then continued to the second inflection point in the pH titration curve. The amount of base consumed between the first and second endpoints is a measure of the number of moles of boric acid complex formed in the sample.

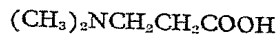
The above description is exemplary of the technique employed to quantitatively and qualitatively identify the groups present. In specific case, analytical techniques may be adapted to a specific resin; however, in each case, consistent with the above description, there exists methods known in the art which yield appropriate accurate determinations of the significant chemical moiety content.

Illustrating the invention are the following examples, which, however, are not to be construed as limiting the invention to their details. All parts and percentages in the examples, as well as throughout this specification are by weight unless otherwise specified.

In several of the examples, there are employed oxyalkylene-containing monoalcohols produced by reacting ethanol with ethylene oxide by using potassium hydroxide catalyst. "Monoalcohol A", as utilized below, is such a reaction product made with 5 moles of ethylene oxide per mole of ethanol and "Monoalcohol B" is the reaction product of 10 moles of ethylene oxide per mole of ethanol.

#### EXAMPLE I

An amine of the formula



was produced from the reaction of dimethylamine (25 percent solution in water) with methyl acrylate, as described in U.S. Patent 3,419,525. This amine (50 parts) was added to a reaction vessel containing 450 parts of Polyepoxide A at 65°C. The temperature rose to 82°C. in 20 minutes; 850 parts of deionized water were slowly added with stirring over a period of 45 minutes. The product was a yellow, clear solution having a solids content of 37.3 percent and an epoxy value of 6361.

The above resin solution after dilution to 10 percent solids with deionized water was electrodeposited using zinc phosphate treated steel electrodes and the following conditions:

Bath temperature	80°F.
pH	6.0
Deposition time	60 seconds
Voltage	400 volts
Current	0.4 amp. max.

There was obtained an adherent coating on the cathode which was then baked at 400°F. for 10 minutes. The cured coating was hard, flexible, and adherent, having a thickness of about 1.2 mil. It was highly resistant to acetone.

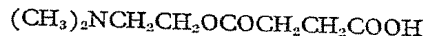
Polyepoxide A is produced by reacting one mole of polypropylene glycol (M.W. about 425) with 2 moles of Epon 834, a bisphenol A-epichlorhydrin epoxy having an average M.W. of about 450 and an epoxide equivalent of 225—290.

#### EXAMPLE II

Example I was repeated except that the cathode employed was aluminum. Similar results were obtained.

#### EXAMPLE III

An amine of the formula



was produced by reacting dimethylethanolamine with succinic anhydride. This amine (4.7 parts) was reacted with 87 parts of Polyepoxide B at 70°C. and diluted with deionized water to a solids content of 59 percent. A 3 mil wet film of this resin solution was drawn on a steel panel and baked at 350°F. for 10 minutes. A hard glossy cured adherent coating was obtained, having excellent solvent resistance.

The resin solution was further diluted to 10 percent solids with deionized water and formic acid added to a pH of 4—5. Electrodeposition of this product using steel electrodes at 250 volts for 90 seconds provided an adherent coating on the cathode. After baking at 350°F. for 10 minutes, the coating had good solvent resistance.

Polyepoxide B is produced by reacting one mole of polypropylene glycol (M.W. about 1500) with 2 moles of Epon 1031, a bisphenol A-epichlorhydrin epoxy having an average M.W. of about 900 and an epoxide equivalent of about 225.

#### EXAMPLE IV

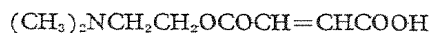
A reaction vessel containing 53.5 parts of Polyepoxide A (80 percent solids in isophorone) was heated to 70°C. There were added 3 parts of an amine produced by reacting dimethylethanolamine with dodecylsuccinic anhydride, and then there were added 6 parts of a second amine produced from dimethylethanolamine and maleic anhydride. During the second addition the temperature was raised to 95°C. and stirring was continued for 15



minutes at this temperature. The product when diluted with water and electrodeposited, as in the above examples, provided an adherent solvent-resistant coating.

#### 5 EXAMPLE V

An amine of the formula



was made by reacting dimethylethanolamine with maleic anhydride. This amine (53 parts) 10 was reacted at 70°C. with 530 parts of an oxyalkylene-modified polyepoxide produced from 400 parts of Epon 834 with 165 parts of polyethylene glycol (molecular weight 400). After the reaction had progressed for 20 15 minutes the temperature was 94°C.; there were added 23 parts of isophorone and 425 parts of deionized water, followed by sufficient aqueous formic acid to make the pH 3.7. Additional water was added to make the solids content 10 percent and the composition electrodeposited, using an aluminum cathode, at 150 volts for 15 seconds; the maximum current was 2.9 amps. An adherent coating was obtained on the cathode which after baking at 400°F. for 30 minutes was hard, glossy and solvent-resistant. 25

#### EXAMPLE VI

An amine of the formula



30 was produced from the reaction of dimethylamine with methyl methacrylate in aqueous solution. Following the procedure of the above examples, 27.8 parts of this amine were reacted with 250 parts of polyepoxide (diglycidyl ether of Bisphenol A, epoxide equivalent 185—200; 35 "Epi-Rez 510") in the presence of 77 parts of the dimethyl ether of diethylene glycol. Water and formic acid were used to reduce the solids content to 5 percent and the pH to 5.9. Electrodeposition of the product on strips of zinc phosphate-treated steel at 200 volts for 20 seconds provided adherent films which after baking at 385°F. for 30 minutes were hard, glossy, extremely solvent-resistant coatings. 45

#### EXAMPLE VII

Into a reactor equipped with stirrer, thermometer; condenser, inlet gas sparge and heating element was charged 500 parts of Epon 840 and 65 parts of isophorone. 50

A salt solution was prepared by admixing 32.5 parts of dimethylethanolamine, 22.5 parts of acetic acid and 15.5 parts of isopropanol. The salt solution was added to the above resin solution beginning at a temperature of 49°C. over a period of 20 minutes, with the tempera- 55

ture ranging from 49°C. to 75°C. After the addition was complete the reaction mixture was held at 75—85°C. for an additional 5 minutes. There was then added 287 parts of deionized water over a 5-minute period to yield the resin solution at a temperature of 62°C. The analysis of the resin, adjusted to 100 percent solids, was as follows:

Epoxy value	650	65
Hydroxyl value	140	
Quaternary acetate groups per gram of resin	0.3644	
Milliequivalents of amine acetate per gram of resin	0.085	70

To 215 parts of the above resin solution was added 1200 parts of deionized water. The resultant electrodeposition bath had a pH of 8.5. Films when electrodeposited at 150 volts were rough, hard films. 75

#### EXAMPLE VIII

This Example illustrates the advantages obtained by the employment of a quaternary ammonium salt of an acid having a dissociation constant greater than  $1 \times 10^{-5}$ . Part A is not an example of the invention but a comparative example. 80

Part A

Into a reactor as described in Example VII were charged 500 parts of Epon 840 and 65 parts of isophorone. A salt solution was prepared from 32.2 parts of dimethylethanolamine and 22.8 parts of boric acid and 15.5 parts of isopropanol and 20 parts of deionized water. The salt solution was added to the above resin solution beginning at a temperature of 55°C. over a 20-minute period with the temperature ranging from 55—76°C. The reaction mixture was held for five minutes at a temperature of 76—85°C. after the addition was complete. There was then added 287 parts of deionized water over a 4-minute period to yield a resin solution at 62°C. The analysis of the resin solution, adjusted to 100 percent solids, was as follows: 100

Epoxy value	573
Hydroxyl value	93

To 215 parts of the above resin solution were added 1200 parts of deionized water to yield an electrodeposition bath with a pH of 9.7. The electrodeposition bath had a rupture voltage of 200 volts. Electrodeposited films were rough and bubbly. The electrodeposition bath had the following analysis: 105

Milliequivalents of quaternary base groups per milliliter	0.0602	110
Milliequivalents of boric acid per milliliter	0.0657	

The electrodeposited film was analyzed to

contain 0.0957 milliequivalents of quaternary borate groups per gram. The wet film contained 63 percent solids.

#### Part B

To 215 parts of the initial resin solution were added 3 parts of 85 percent lactic acid and 1200 parts of deionized water to yield an electrodeposition bath having a pH of 8.5. Films electrodeposited under the same conditions as previously showed improved film appearance and resulted in a uniform film on baking. The electrodeposition bath was analyzed to contain:

15	Milliequivalents of quaternary base per milliliter	0.0617
	Milliequivalents of lactic acid per milliliter	0.0337
	Milliequivalents of boric acid per milliliter	0.0693

The wet electrodeposited film was analyzed to contain 0.1474 milliequivalents of quaternary borate groups per gram. The wet film had a solids content of 66.9 percent.

#### EXAMPLE IX

Into a reactor as described in Example VII was charged 500 parts of Epon 834. The resin was heated to 80°C. A salt solution comprising 112.3 parts of 40% dimethylamine in water, and 106 parts of 85% lactic acid in water, having a pH of 4.3, was added at a temperature of 80—85°C. over a 20 minute period. The reaction mixture was then heated to 97°C. and refluxed for 20 minutes. There was then added 169 parts of deionized water, followed by 100 parts in ethyl Cellosolve and 10 parts of 90% formic acid. The resin dispersion was somewhat cloudy. There was then added to the resin dispersion sufficient water to form a 10 percent solids bath. Sufficient formic acid was added to adjust the pH to 2.5.

An aluminum strip was electrocoated at a bath temperature of 80°F. at 100 volts for 60 seconds. The film was deposited on the cathode, which was baked at 350°F. for 20 minutes. A glossy, hard yellow film was obtained.

The resin at 100 percent solids had the following properties:

50	Epoxy value	1160
	Hydroxyl value	141

The electrodeposition bath analyzed to contain:

55	Milliequivalents of amine per gram of resin	0.2145
	Milliequivalents of quaternary base groups per gram of resin	0.2830
	Milliequivalents of acid per gram of resin	0.4980

#### EXAMPLE X

Into a reactor as described in Example VII was charged 500 parts of Epon 834. This resin was heated to 80°C. and there was added a salt solution formed by admixing 101 parts of dipropylamine and 106 parts 85 percent lactic acid, together with 33 parts of isopropanol. The salt solution was added at 80—85°C. with heat over a 20 minute period. After the addition was complete, the reaction mixture was heated to 95°C. and refluxed for 20 minutes. 167 parts of deionized water were then added. A cloudy resin dispersion was obtained, to which was added 100 parts ethyl Cellosolve, 10 parts of 90 percent formic acid. A clear yellow resin solution was obtained.

Analysis of the product adjusted to 100 percent solids is as follows:

Epoxy value	1120
Hydroxyl value	143

The resin was analyzed to contain:

80	Milliequivalents of amine per gram of resin	0.0675
	Milliequivalents of quaternary base groups per gram of resin	0.4310
85	Milliequivalents of acid per gram of resin	0.4985

Useful electrodeposited films were obtained.

#### EXAMPLE XI

Into a reactor equipped with stirrer, thermometer condenser, inert gas inlet and heating element was charged 1,005 parts of Epon 829 and 339 parts of bisphenol-A. The mixture was heated to 180°C. and held for 45 minutes at 180—188°C. There was then added at 120°C. 114 parts of isopropanol and the mixture cooled to 79°C. There was then added 141.0 parts of a 75 percent solids solution in isopropanol of dimethylethanolamine lactate over a 20 minute period between 79°C. and 93°C. with heating. The reaction mixture was held at 93°C.—97°C. for two additional minutes, and there was then added 425 parts of deionized water over a four minute period at which time the temperature was 75°C.

There was then added a solution of 7 parts of Foam Kill 639 in 90 parts of 2-ethylhexanol. A clear yellow resin solution was obtained. This is hereinafter referred to as the base resin.

Analysis	(100% solids)	110
Epoxy value	1085	
Hydroxyl value	233	

To 272 parts of the base resin was added 1630 parts of deionized water to yield a 10 percent solids electrodeposition bath with a pH of 6.7. Zinc phosphate steel panels were

electrocoated at 250 volts for 90 seconds at 80°F. Uniform film build was noted. The film was baked at 350°F. for 30 minutes to yield a glossy film, 0.45 mils, pencil hardness 6H.

5 Film electrocoated at 300 volts for 90 seconds at 80°F. and baked as above yielded 0.5 mils pencil hardness 6H.

To the same bath was added 6.6 parts of boric acid. The bath had a pH of 6.4. Film  
10 electrocoated and baked as above yielded:

250 volts—0.5 mils, 7H+ pencil

300 volts—0.6 mils, 7H+ pencil

#### EXAMPLE XII

15 Into a reactor equipped with stirrer, reflux condenser, thermometer and heating means was charged 2070 parts of Epon 834, 875 parts of polypropylene glycol with an average molecular weight of 400—425 (PPG 425) and 7 parts of dimethylethanolamine. The reaction mixture was heated to 130—138°C. for 5½ hours, at which time the reaction product had a Gardner-Holdt viscosity of H- (measured as a 50 percent solids in a 90/10 isophorone/toluene mixture). There was then  
20 added 4.2 parts of 90 percent formic acid to neutralize the dimethylethanolamine catalyst. At this point the product had an epoxide equivalent of 800 and hydroxyl value of 269. This resin is hereinafter referred to as the base resin of Example XII.

To 500 parts of the above resin was added a salt solution prepared by admixing 33.2 parts of dibutylamine, 28 parts of an 85-percent lactic acid solution, and 14 parts of isopropanol. This salt solution was added over a 20 minute period at a temperature between 70—87°C. The reaction mixture was then held for an additional 5 minutes at a temperature between 87—90°C. There was then added  
35 315 parts of deionized water. A pearlescent resin was obtained.

This product contained 0.249 milliequivalents of quaternary base groups per gram, 0.055 milliequivalents of amine per gram and  
45 0.328 milliequivalents of lactic acid per gram. The analyzed resin properties, adjusted to 100 percent solids, showed an epoxide equivalent of 1300 and a hydroxyl value of 108.

#### EXAMPLE XIII

50 To 500 parts of the base resin of Example XII, was added a mixture of 25 parts of 1-amino-2-propanol, 35.3 parts of 85 percent lactic acid solution and 14.0 parts of isopropanol. This mixture was added to the resin at a temperature of 70—89°C. over a 20 minute period. The reaction mixture was held for an additional 5 minutes, the temperature increasing to 97°C. There was then added 315 parts of deionized water to produce a pearlescent dispersion. The resultant product had the following analysis: 0.159 milliequivalents of quaternary base groups per

gram; 0.133 milliequivalents of amine per gram and 0.327 milliequivalents of lactic acid per gram. The 100 percent solids resin was analyzed and calculated to have an epoxide value of 1590 and a hydroxyl value of 131.

#### EXAMPLE XIV

In the manner of Example XII, there was reacted 1770 parts of Epon 829, and 302 parts of Bisphenol A, which were heated to 170°C., at which time an exotherm was noted to 190°C. The temperature was controlled between 180—185°C. for 45 minutes. The reaction mixture was then cooled to 100°C and 790 parts of polypropylene glycol with an average molecular weight of 600, together with 5 parts of dimethyl ethanolamine were added. The reaction mixture was then heated from 130 to 139°C. to a Gardner-Holdt viscosity of M (measured at 50 percent solids in a 90/10 isophorone/toluene mixture). This required a reaction time of approximately 7 hours. The reaction mixture was then cooled to 117°C. and 3.5 parts of a 90 percent formic acid solution was added. The product had an epoxide equivalent of 1000 and a hydroxyl value of 302.

The reaction mixture was then cooled to 73°C. and there was added 327 parts of dimethylethanolamine hydrochloride salt at 66 percent solids in water. The salt was added over a 20 minute period at a temperature between 73—92°C. The reaction mixture was held for an additional two minutes at 92—97°C. There was then added 200 parts of 2-ethylhexanol and 15.5 parts of Foam Kill 639. After mixing, there was added an additional 840 parts of deionized water, electrodepositable composition had a pH of 8.2 and a measured and calculated value based on 100 percent solids: epoxide equivalent of 3950 and a hydroxyl value of 69.4.

The following analyses were obtained: 0.486 milliequivalents of quaternary base groups per gram; 0.411 milliequivalents of chloride per gram; and 0.075 milliequivalents of formic acid per gram.

#### EXAMPLE XV

In the manner of Example XII there was reacted 1890 parts of Epon 829 and 180 parts of Bisphenol A. The mixture was heated to 170°C., at which time an exotherm was noted. The temperature was controlled between 180—185°C. for 45 minutes. The reaction mixture was then cooled to 100°C. and there was then added 875 parts of polypropylene glycol 425 (average molecular weight 400—425), along with 8 parts of dimethylethanolamine. The reaction mixture was held at 130—137°C. for 4.5 hours to obtain a Gardner-Holdt viscosity of L, measured at a 50 percent solids solution in a 90/10 isophorone/toluene mixture). There was then added 9.6 grams of 90 percent formic acid.

To 500 parts of the above resin there was then added a salt formed by mixing 25.8 parts of triethylamine and 24.2 parts of 36 percent hydrochloric acid. This salt was added over a 15 minute period at temperatures from 70—89°C. The reaction mixture was held at 89°C. for an additional three minutes and there was added 295 parts of deionized water. The analyzed calculated values, based on 100 percent solids were: an epoxide equivalent of 3660 and a hydroxyl value of 72.5. This resin is hereinafter referred to as the base resin of Example XV.

The above mixture was reduced to 10 percent solids with deionized water to a pH of 8.1. Aluminum metal strip was coated for 30 seconds at 100 volts at a bath temperature of 75°C., the resultant electrodeposited film was baked at 350°F. for 20 minutes to produce an acetone-resistant film.

To 440 parts of the above base resin was added 95 parts of butylbenzylphthalate, 19.0 parts of 2-ethylhexanol, and 1.9 parts of Foam Kill 639. There was then added 3250 parts of deionized water. The resultant electrodepositable compositions had a pH of 8.9. Zinc-phosphated steel panels were coated at 250 volts for 90 seconds at a bath temperature of 80°F. The resultant electrodeposited film was baked at 350°F. for 20 minutes, yielding a film build of 0.8 mils, a 3H pencil hardness.

The above 8.5 percent solids electrodepositable composition analyzed as follows: 0.0312 milliequivalents of quaternary base groups per milliliter, 0.0251 milliequivalents of chloride per milliliter. The wet electrodepositable film was analyzed to contain 85.8 percent solids and 0.247 milliequivalents of amine per gram, and contained no chloride.

#### EXAMPLE XVI

Into a reactor equipped with stirrer, reflux condenser, thermometer, and heating means was charged 1890 parts of Epon 829 and 180 parts of Bisphenol A. The mixture was heated to 170°C., at which time an exotherm was noted to 180°C. The reaction mixture was held between 180—190°C. for 45 minutes. The reaction mixture was then cooled to 130°C. There was added a mixture of 875 parts of polypropylene glycol 425 and 8 parts of dimethylethanolamine. The reaction mixture was heated between 130—137°C. for approximately 5½ hours to a Gardner-Holdt viscosity of J+, measured in a 50% solids solution 90/10 isophorone/toluene. There was then added 9.6 parts of 90 percent formic acid.

The reaction mixture was cooled to 70°C. To 500 parts of the above at 70°C. was added the following salt solution comprised of 18 parts of boric acid, 25.3 parts of dimethylethanolamine and 11 parts of isopropanol. The salt solution was added over an 18 minute period at a temperature of between 70—

90°C. There was then added 276 parts of water and the mixture held at 75°C. for 5 minutes. There was then added a solution of 34.5 parts of 2-ethylhexanol and 2.7 parts of Foam Kill 639. The resin analysis converted to 100 percent showed an epoxide equivalent of 920 and a hydroxyl value of 71.

To 220 parts of the above resin solution was added 47.5 parts of butylbenzylphthalate and the mixture reduced to 5.75 percent solids with deionized water. The electrodepositable composition had a pH of 7.6.

The above composition was electrocoated at 250 volts for 90 seconds at a bath temperature of 80°C. on zinc-phosphated steel panel.

The electrodepositable bath was analyzed as follows: 0.0235 milliequivalents of quaternary base per milliliter; 0.0074 milliequivalents of weak acid per milliliter and 0.0255 milliequivalents of boron per milliliter. The wet electrodeposited film was analyzed to contain 75.1 percent solids and to contain 0.062 milliequivalents of quaternary borate per gram of wet film and 0.188 milliequivalents of amine per gram of wet film.

#### EXAMPLE XVII

In the manner of Example XVI there was reacted 1135 parts of Epon 829, and 10 parts of Bisphenol A. After a reaction time of 50 minutes, there was added 525 parts of polypropylene glycol 425 and 4.2 parts of dimethylethanolamine. The reaction mixture was held at 130—137°C. for 5½ hours to a Gardner-Holdt viscosity of H+, measured as a 50% solution in a 90/10 isophorone/toluene mixture. The reaction mixture was cooled to 123°C. and 5.1 parts of 90 percent formic acid was added. The reaction mixture was further cooled to 71°C. and there was added a mixture of 51.6 parts of dimethylethanolamine, 61.3 parts of an 85 percent lactic acid solution and 60.3 parts of neopentyl glycol. The salt solution was added over a 20 minute period at a temperature of 71—79°C. The reaction mixture was held for an additional 5 minutes at 79—91°C. There was then added 1000 parts of deionized water. The analysis adjusted to 100 percent solids showed an epoxide equivalent of 1270, a hydroxyl value of 116 and an acid value of 0. This resin is hereinafter referred to as the base resin of Example XVII.

To 433 parts of the base resin of Example XVII was added 95 parts of butylbenzylphthalate, 19 parts of 2-ethyl hexanol and 3250 parts of water. The resulting electrodepositable composition had a pH of 5.6. The composition was electrodeposited on zinc phosphated steel panels at 250 volts for 90 seconds at a bath temperature of 80°F. The electrodeposited film was baked at 350°F. for 20 minutes. The resultant electrodeposited film was smooth and glossy and had a pencil hardness of H.

To 435 parts of the base resin of Example XVII was added 95 parts of butylbenzylphthalate, 8.9 parts of trimethoxyboroxine, 20 parts of 2-ethylhexanol and 2 parts of Foam Kill 639. There was then added 3250 parts of deionized water, yielding a white pearlescent dispersion having a pH of 5.6.

Zinc phosphated steel panels were electrodeposited in the above bath at 250 volts for 90 seconds at a bath temperature of 80°F. The resultant electrodeposited films were baked at 350°F. for 20 minutes to yield a film build of 0.9 to 1 mil at a 4H+ pencil hardness and a throw power of 2-11/16 inches.

The above electrodeposition bath at 9.2 percent solids was analyzed to contain 0.0238 milliequivalents of quaternary base for milliliter; 0.0243 milliequivalents of lactic acid per milliliter and 0.050 milliequivalents of boron per milliliter.

#### EXAMPLE XVIII

In the manner of Example XVI there was reacted 1890 parts of Epon 828, 180 parts of Bisphenol A, at a temperature of 175°C. to 180°C. for 45 minutes. The reaction mixture was then cooled to 130°C. and there was then added 875 parts of polypropylene glycol 425 and 7 parts of dimethylethanolamine. The reaction mixture was heated to 130—138°C. for five hours to a Gardner-Holdt viscosity of H+ measured in 50 percent solids solution of 90/10 isophorone/toluene. The reaction mixture was cooled to 121°C. and there was added 4.8 grams of 90 percent formic acid. The reaction mixture was cooled to 73°C. At this point the product had an epoxide equivalent of 763 and a hydroxyl value of 348. To the above mixture was added a salt solution formed by combining 106 parts of dimethyl ethanolamine, 129 parts of 85 percent solids lactic acid solution and 53.9 parts of isopropanol. The salt solution was added over a period of 18 minutes at a temperature of 73—80°C. The reaction mixture was held for an additional 7 minutes at 80°C. to 100°C. at which time there was added 500 milliliters of deionized water and a solution of 208 parts of 2-ethylhexanol containing 15.5 parts of Foam Kill 639. There was then added an additional 960 parts of water. The resultant composition analyzed, adjusted to 100 percent solids, an epoxide equivalent of 1460 and a hydroxyl value of 132.5. This resin solution is hereinafter identified as the base resin of Example XVIII.

To 220 parts of the base resin of Example XVIII was added 47.5 parts of butylbenzylphthalate and 1630 parts of water. The resultant electrodepositable composition had a pH of 8.5. The composition was electrodeposited on zinc phosphate steel panels at 250 volts for 90 seconds at a bath temperature of 80°F. The resultant electrodeposited film

was baked at 350°F. for 20 minutes to yield a film build of 0.65 mils at a 2H pencil hardness. The films were smooth and glossy and the composition had a 2 inch throw power.

To 220 parts of the base resin of Example XVIII was added 45 parts of butylbenzylphthalate, 2 parts of boric acid and 1675 parts of deionized water. The resultant electrodepositable composition had a pH of 5.7. The composition was electrodeposited and baked in the same manner as above to yield a film build of 0.9 mils at a 4H+ pencil hardness. The composition had a 2-3/4 inch throw power.

To 220 parts of the base resin of Example XVIII was added 45 parts of butylbenzylphthalate, 6.0 parts of boric acid and 1675 parts of water. The resultant electrodepositable composition had a pH of 5.7. The composition was electrodeposited and baked in the same manner as above to yield a film build of 0.8 mils, a 5H pencil hardness and a throw power of 2-7/8 inches.

#### EXAMPLE XIX

In the manner of Example XII there was reacted 400 parts of Epon 834 and 175 parts of propylene glycol 425, together with 1.4 parts of dimethylethanolamine. This mixture was reacted for 5 hours at a temperature of between 130—139°C. to an H+ Gardner-Holdt viscosity measured in 50 percent solids solution of a 90/10 isophorone/toluene mixture. The reaction mixture was cooled to 122°C. and there was then added one part of 90 percent formic acid. The resultant product had an epoxide equivalent of 985 and a hydroxyl value of 321. The reaction mixture was cooled to 69°C. and there was added a salt solution formed by admixing 106 parts of 85 percent lactic acid, 59 parts trimethylamine and 41 parts of isopropanol. 55 parts of this salt solution was added over a 19 minute period at a temperature of 69—80°C. The mixture was held for an additional five minutes at 86—91°C. There was then added 430 parts of deionized water. The product analyzed, adjusted to 100 percent solids, to have an epoxide equivalent of 1930 and a hydroxyl value of 81.5. This resin is hereinafter identified as the base resin of Example XIX.

To 200 parts of the base resin of Example XIX was added 45 parts of butylbenzylphthalate, 9.5 parts of 2-ethylhexanol, and 5.9 parts of Foam Kill 639, followed by 1630 parts of deionized water. The resultant electrodepositable composition had a pH of 4.65.

Zinc phosphated steel panels were electrodeposited at 250 volts for 90 seconds at a bath temperature of 80°F. The electrodeposited films were baked at 350°F. for 20 minutes to yield smooth, hard, glossy films.

The electrodepositable bath at 9.9 percent solids analyzed to contain 0.0266 milliequiva-

lents of quaternary base groups per milliliter, 0.0019 milliequivalents of amine per milliliter and 0.0325 milliequivalents of lactic acid per milliliter. The wet electrodeposited film contained 70.6 percent solids and analyzed to contain 0.190 milliequivalents of amine per gram of wet film.

#### EXAMPLE XX

In the manner of Example XVI there was reacted 1890 parts of Epon 829, 180 parts of Bisphenol A at a temperature of 175—180°C. for 30 minutes. There was then added 875 parts of polypropylene glycol 445 and the temperature reduced to 130°C. There was added 8 parts of dimethylethanolamine and the reaction mixture heated at 130—140°C. for a period of 5-1/2 hours to a Gardner-Holdt viscosity of H+ measured at 50 percent solids solution in a 90/10 isophorone/toluene mixture. The reaction mixture was cooled to 116°C. and there was added 9.6 parts of 90 percent formic acid.

To 500 parts of the above resin at 60—70°C. was added 15 parts dimethylethanolamine over a 9 minute period. After an additional minute at 73°C. there was added 17.8 parts of lactic acid over a 10 minute period at a temperature of 73—78°C. The reaction mixture was held at 75°C. for 3 minutes. There was then added 17.4 parts of neopentyl glycol and the reaction mixture held for 2 minutes at 71°C. There was then added 9.8 parts of boric acid. The reaction mixture held for a short time at 75—77°C. There was then added 30 parts of deionized water. The resultant resin analyzed, adjusted to 100 percent solids, to have an epoxide equivalent of 1285 and an acid value of 16.4 and a hydroxyl value of 107.8. The resin is hereinafter referred to as the base resin of Example XX.

To 440 parts of the base resin of Example XX was added 95 parts of butylbenzylphthalate, 19 parts of 2-ethylhexanol and 1.9 parts of Foam Kill 639. There was then added 3250 parts of deionized water.

The resultant electrodepositable composition was electrodeposited on zinc phosphated steel panels at 250 volts for 90 seconds at a bath temperature of 80°F. The electrodeposited film was baked at 350°F. for 20 minutes to yield a film build of 0.7—0.8 mils of smooth, hard, glossy film having a pencil hardness of 4H+.

#### EXAMPLE XXI

To 500 parts of the resin adduct of paragraph 1 of Example XX were added 18.6 parts of lactic acid (85 percent solution) and 19.4 parts of triethylamine. The addition was made over a 19 minute period at a temperature of 70—85°C. The reaction mixture was held an additional 5 minutes at 85—90°C. The resultant resin was analyzed to have an

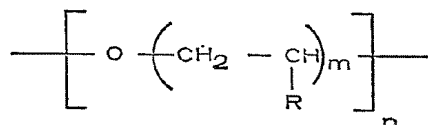
epoxide equivalent of 2790 and a hydroxyl value of 105.

To 440 parts of the above resin was added 95.0 parts of butylbenzylphthalate, 19 parts of 2-ethylhexanol and 1.9 parts of Foam Kill 639. There was then added 3250 parts of deionized water.

The resultant electrodepositable composition was electrodeposited on zinc phosphated steel panels at 250 volts for 90 seconds at 80°F. bath temperature. The electrodeposited film was baked at 350°F. for 20 minutes to yield a film build of 0.5—0.6 mils of smooth glossy film having a 3H pencil hardness.

In Specification No. 1,306,101 there is claimed a resinous composition comprising an ungelled reaction product of:

(a) an epoxy compound containing oxyalkylene groups of the formula



where R is hydrogen or alkyl and n and m are numbers, and

(b) a boron ester substituted with at least one amino group.

In Specification No. 1,306,102 there is claimed a method of coating an electrically conductive substrate which comprises passing electric current between an anode and a cathode in contact with a water dispersed composition in which the major component is an ungelled reaction product of (a) an epoxy compound and (b) a boron ester substituted with at least one amino group, whereby an adherent coating of said composition is deposited on the cathode.

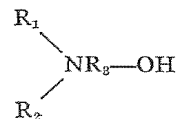
We make no claim wherein to any resin or aqueous dispersion of a resin which is or is derived from the reaction product of an epoxy compound with a boron ester containing one or more amino groups, or to any method for preparing such resin or aqueous dispersion by means of the reaction of an epoxy compound with such boron ester. Likewise we make no claim to any method of electrodepositing a coating from such aqueous dispersion or to any coating or coated object produced by means of such electrodeposition method.

#### WHAT WE CLAIM IS:—

1. A ungelled water-dispersible epoxy resin having in the resin molecule:

- (A) more than one 1,2-epoxy group; and
- (B) at least 0.05 percent by weight of chemically-bound nitrogen, at least one percent of which is in the form of a quaternary ammonium base salt; and when said ammonium base salt is of an

- acid having a dissociation constant of  $1 \times 10^{-6}$  or less  
(C) at least 1 percent by weight of oxyalkylene groups.
- 5 2. A resin as claimed in claim 1 which contains 0.05 to 16 percent by weight of chemically-bound nitrogen.
3. A resin as claimed in claim 1 or 2 wherein at least 20 percent of the nitrogen is in the form of a quaternary ammonium base salt.
- 10 4. A resin as claimed in claim 3 wherein at least 50 percent of the nitrogen is in the form of a quaternary ammonium base salt.
- 15 5. A resin as claimed in claim 4 wherein substantially all of the nitrogen is in the form of a quaternary ammonium base salt.
6. A resin according to any preceding claim in which the resin contains less than 1 percent by weight of oxyalkylene groups and the quaternary ammonium base salt is a salt of an acid having a dissociation constant greater than  $1 \times 10^{-5}$ .
- 20 7. A resin according to claim 6 in which the acid is lactic acid.
- 25 8. A resin according to any of claims 1 to 5 in which the resin contains at least 1 percent by weight of oxyalkylene groups.
9. A resin as claimed in claim 8 wherein the quaternary ammonium base salt is a salt of boric acid or an acid having a dissociation constant greater than that of boric acid.
- 30 10. A resin as claimed in claim 9 wherein the acid has a dissociation constant greater than  $1 \times 10^{-5}$ .
- 35 11. A resin as claimed in claim 10 wherein the acid is lactic acid.
12. A resin as claimed in any preceding claim which also contains chemically-bound boron.
- 40 13. A mixture comprising a resin as claimed in any preceding claim and boric acid or a compound hydrolysable to form boric acid.
14. An aqueous dispersion comprising an ungelled water-dispersed epoxy resin having in the resin molecule:
- 45 (A) more than one 1,2-epoxy group;  
(B) at least 0.05 percent by weight of chemically-bound nitrogen, at least 1% of which is in the form of a quaternary ammonium base salt; and when said ammonium base salt is of an acid having a dissociation constant of  $1 \times 10^{-5}$  or less  
(C) at least 1% by weight of oxyalkylene groups.
- 50 15. An aqueous dispersion as claimed in claim 14 wherein the resin contains 0.05 to 16 percent by weight of chemically-bound nitrogen.
- 60 16. An aqueous dispersion as claimed in claim 14 or 15 wherein at least 20 percent of the nitrogen is in the form of a quaternary ammonium base salt.
17. An aqueous dispersion as claimed in claim 16 wherein at least 50 percent of the nitrogen is in the form of a quaternary ammonium base salt.
18. An aqueous dispersion as claimed in claim 17 wherein substantially all of the nitrogen is in the form of a quaternary ammonium base salt.
- 70 19. An aqueous dispersion as claimed in any of claims 14 to 18 wherein the salt is a salt of boric acid or an acid having a dissociation constant greater than that of boric acid.
20. An aqueous dispersion as claimed in claim 19 wherein the acid has a dissociation constant greater than  $1 \times 10^{-5}$ .
21. An aqueous dispersion as claimed in claim 20 wherein the acid is lactic acid.
- 80 22. An aqueous dispersion as claimed in any of claims 14—21 which also contains boron.
23. An aqueous dispersion as claimed in claim 22 which contains from 0.01—8 percent by weight of boron present as boric acid and/or a borate or a boron complex.
- 85 24. An aqueous dispersion as claimed in any of claims 14 to 23 which contains 1—25 percent by weight of the resin.
25. An aqueous dispersion as claimed in any of claims 14 to 24 which also contains a coupling solvent.
- 90 26. An aqueous dispersion as claimed in claim 25 wherein the coupling solvent comprises 2-ethyl hexanol.
27. A method of preparing an ungelled water dispersible epoxy resin according to claim 1 which comprises reacting a polyepoxide with an amine salt.
- 95 28. A method as claimed in claim 27 wherein the polyepoxide contains at least 5 percent by weight of oxyalkylene groups.
29. A method as claimed in claim 27 or 28 wherein the acid has a dissociation constant greater than  $1 \times 10^{-5}$ .
- 100 30. A method as claimed in claim 29 wherein the acid is lactic acid.
31. A method as claimed in any of claims 27 to 30 wherein the amine salt is a salt of an amine containing one or more secondary or tertiary amino groups and at least one hydroxyl group.
- 110 32. A method as claimed in claim 31 wherein the amine corresponds to the formula:
- 115



where

$R_1$  is hydrogen or an alkyl, aryl, alkaryl or aralkyl group,

$R_2$  is an alkyl, aryl, alkaryl or aralkyl group, and

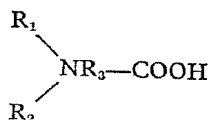
$R_3$  is a divalent organic group.

33. A method as claimed in claim 32 wherein the amine is dimethylethanolamine or diethylethanolamine.

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34. A method as claimed in any of claims 27 to 30 wherein the amine salt is or is a salt of an amine containing one or more secondary or tertiary amino groups and at least one terminal carboxyl group.

35. A method as claimed in claim 34 wherein the amine corresponds to the formula



where

$R_1$ ,  $R_2$  and  $R_3$  are as defined in claim 32.

36. A method as claimed in any of claims 27 to 35 wherein the amine salt is a salt of a tertiary amine.

37. An ungelled water-dispersible epoxy resin according to claim 1 when prepared by a method according to any of claims 27 to 36.

38. A method of preparing an aqueous dispersion according to claim 14 which comprises reacting a polyepoxide with an amine salt.

39. A method as claimed in claim 38 wherein the polyepoxide contains at least 5 percent by weight of oxyalkylene groups.

40. A method as claimed in claim 38 or 39 wherein the amine salt is a salt of an acid having a dissociation constant greater than  $1 \times 10^{-5}$ .

41. A method as claimed in claim 40 wherein the acid is lactic acid.

42. A method as claimed in any of claims 38 to 41 wherein the amine salt is as specified in claim 31.

43. A method as claimed in claim 42 wherein the amine salt is a salt of an amine as specified in claim 32.

44. A method as claimed in claim 43 wherein the amine salt is a salt of dimethylethanolamine or diethylethanolamine.

45. A method as claimed in any of claims 38 to 41 wherein the amine salt is as specified in claim 34.

46. A method as claimed in claim 45 wherein the amine is as specified in claim 35.

47. A method as claimed in any of claims 38 to 46 wherein the amine salt is a salt of a tertiary amine.

48. An aqueous dispersion according to claim 14 when prepared by a method in accordance with any of claims 38 to 47.

49. A method of coating a conductive substrate serving as a cathode which comprises passing an electric current between an anode and said cathode in electrical contact with an aqueous dispersion in accordance with any of claims 14 to 26 or 48.

50. A method according to claim 49 wherein the aqueous dispersion has a pH in the range of 3.0 to 8.5.

51. An article comprising a conductive substrate when coated by a method according to claim 49 or 50.

52. An uncured electrodeposited coating on an electrically conductive substrate which comprises an ungelled epoxy resin having in the molecule more than one 1,2-epoxy group, at least 0.05 percent by weight of chemically-bound nitrogen at least 1 percent of which is in the form of quaternary ammonium base groups, and at least 1 percent by weight of oxyalkylene groups.

53. An uncured coating as claimed in claim 52 which contains boron.

54. An uncured coating as claimed in claim 53 which contains 0.01—8 percent by weight of boron in the form of quaternary and/or amine borates or boron complexes.

55. An ungelled water-dispersible epoxy resin as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the Examples.

56. An aqueous dispersion as claimed in claim 14 and substantially as hereinbefore described with reference to any one of the Examples.

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